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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Sascha Kreiskott	Docket No.:	S-99,952
Serial No.:	10/624,350	Examiner:	M. Alexander
Filed :	7/21/2003	Art Unit:	1742

For : HIGH CURRENT DENSITY ELECTROPOLISHING IN THE PREPARATION OF HIGHLY SMOOTH SUBSTRATE TAPES FOR COATED CONDUCTORS

Customer No. 35068

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DECLARATION OF PRIOR INVENTION IN THE UNITED STATES OR IN A NAFTA OR WTO MEMBER COUNTRY TO OVERCOME CITED PATENT OR PUBLICATION (37 C.F.R. § 1.131)

Sir:

Purpose of Declaration

1. This declaration is to establish completion of the invention of this application in

☒ the United States

☐ the NAFTA country ____________________(name of country)

☐ the WIPO country ______________________(name of country)

at a date prior to ___July 1, 2003____, that is the effective date of the prior art

☐ publication ____

☐ patent ____

☒ patent publication _______2005/0000826 by Qiao_____________________

☐ other ____

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that was cited by the

☒ examiner.

☐ applicant.

2. The person making this declaration is:

☐ the inventors.

☒ only some of the joint inventors (and a suitable excuse is attached for failure of the omitted joint inventor is attached)

☐ the party in interest (and a suitable explanation as why it is not possible to produce the declaration of the inventors is attached)

Facts and Documentary Evidence

3. To establish the date of completion of the invention of this application, the following attached documents and/or models are submitted as evidence:

(check all applicable items below)

☐ sketches

☐ blueprints

☐ photographs

☐ reproduction(s) of notebook entries

☐ model

☐ supporting statement(s) by witness(es) (where verbal disclosures are the evidence relied upon)

☐ interference testimony

☐ disclosure documents

☒ publication, Kreiskott et al., "Continuous Electropolishing of Hastelloy Substrates for Ion-Beam Assisted Deposition of MgO," Supercond. Sci. Technol. 16 (2003) 613-616.

4. From these documents and/or models, it can be seen that the invention in this application was made

☒ on __or before 25 February 2003__.

☒ at least by the date of __25 February 2003__, which is a date earlier than the effective date of the reference.

Diligence

5. Attached is a statement establishing the diligence of the applicants, from the time of their conception, to a time just prior to the date of the reference, up to the:

☐ actual reduction to practice.

☐ filing of this application.

Time of Presentation of the Declaration

(a) ☒ This declaration is submitted prior to final rejection.

(b) ☐ This declaration is submitted with the first response after final rejection, and is for the purpose of overcoming a new ground of rejection or requirement made in the final rejection.

(c) ☐ This declaration is submitted after final rejection. A showing under 37 C.F.R. § 1.116(b) is submitted herewith.

Declaration

6. As a person signing below:

I herby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the united States code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signatures

7.

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Continuous electropolishing of Hastelloy substrates for ion-beam assisted deposition of MgO

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Abstract
We demonstrate the applicability of continuous electropolishing for the preparation of metal tapes for ion-beam assisted deposition of MgO for the fabrication of in-plane textured template layers. These templates are used for the fabrication of second generation high temperature superconducting wires utilizing $YBa_2Cu_3O_{7-\delta}$ coatings on metallic substrates. Surface roughness values below 1 nm and local slopes of less than 1° could be achieved with the electropolishing process. Mean surface roughness values are lower with the use of electropolishing and slopes of surface roughness inclines are significantly reduced compared to the best results of mechanical polishing (3.5 nm and 5°, respectively). The cost-effective process of electropolishing shows great promise for the fabrication of second generation high temperature superconducting wire.

1. Introduction

Commercial applications of high temperature superconducting wires require fast and cost-effective production processes. Several ways to produce high quality biaxially textured $YBa_2Cu_3O_{7-\delta}$ (YBCO) layers on metal substrates, also known as coated conductors (CC), have been studied during the last few years [1–3]. A promising technique is the ion-beam assisted deposition of MgO (IBAD-MgO) on polycrystalline Ni alloys, such as Hastelloy C-276 tapes, to form a biaxially aligned template layer [4]. The fabrication of CC following this IBAD-MgO approach involves several process steps. After the polishing and cleaning of the tape an amorphous yttria (Y_2O_3) or other seed layers are deposited followed by the IBAD-MgO. In the next process steps, a buffer layer, such as $SrRuO_3$ or $SrTiO_3$, and a final YBCO layer are added by pulsed laser deposition (PLD). Details of our processing techniques are described elsewhere [4, 5]. IBAD-MgO needs very smooth substrate surfaces with shallow local and overall slopes to obtain good in-plane alignment [6]. This necessity is related to the main advantage of the process: the texture is developed in the first 10 nm of the IBAD layer. Therefore, roughness and substrate features on a nm-scale hinder the formation of a good in-plane texture. In comparison, the successful YSZ-IBAD approach needs YSZ layers of 1 μm thickness [7], which increases the deposition time for the template layer by a factor of 100, but the process is less susceptible to substrate tape roughness.

Up to now, tapes smooth on a nm-scale were only demonstrated by the slow (processing speed is few metres per hour), and therefore costly, process of mechanical polishing, which is not easily scaled up to high-throughput production. This was the prime motivation to use electropolishing (EP) as a faster and cheaper process for the finishing of the tape's surfaces. EP utilizes the local increase of the electrical field at protrusions in conducting surfaces. The increased electrical field yields in higher local current densities into the acidic electrolyte and therefore a stronger local etching at the protrusions.

EP offers the opportunity to polish metal substrates at higher speeds than mechanical polishing (tens of metres per hour), and many tapes can be run in parallel through a polishing bath, or wider rolls can be used. Currently, the scalability of the EP process is still limited by the fact that the polishing current is fed into the tape by mechanical contacts outside the polishing bath. Because of the high resistivity of the substrate tapes there is a maximum current at which the resistive losses in the tape cause strong heating, up to several hundred degree celsius

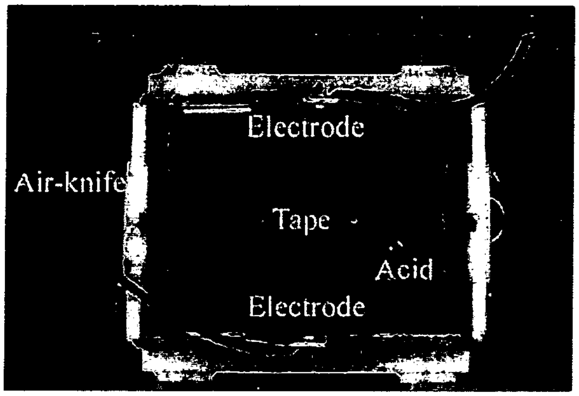

Figure 1. Set-up of the electropolishing station. The inner length of the acid bath is 30 cm.

and therefore uncontrollable substrate-acid reactions. This maximum current limits the possible length of the polishing bath because high polishing current densities are needed to obtain good results and the polishing current density decreases with increasing bath length for a given current through the tape. This issue will be overcome in a new set-up where the mechanical contacts are replaced by electrolytic contacts. In this set-up the tape stays in the acid bath for both contacting and polishing, which prevents an overheating in a wide range of used currents. By the right combination of contacting anodes and polishing cathodes any polishing bath length and area can be realized, which allows a very easy scale-up of the process.

2. Experimental details

The EP research set-up for the continuous polishing of tape was custom made by a commercial supplier[1]. It consists of several modules for cleaning, polishing, rinsing and electroplating of tape. In our experiments, only the polishing station and some of the rinsing stations were used. Figure 1 shows a picture of the EP station. The acid bath has a length of 30 cm. The heated acid is pumped from the sump tank into the EP cell and leaves it through an overflow port. This ensures sufficient acid circulation. The temperature of the acid is controlled between room temperature and 100 °C by a heater system. Air knives blow away the acid after the acid bath. The acid is a proprietary mixture of highly concentrated phosphoric and sulphuric acid and some other minor ingredients[2]. In the next process step, the tape is rinsed several times with deionized water at room temperature and dried in an air stream. The polishing voltage is applied to the tape through brass brush contacts on both sides of the bath, about 20 cm away from the side walls of the bath (not shown in figure 1). Gold-plated electrodes in the acid bath close the electrical circuit. With the existing contact brushes, voltages up to 12 V can be applied. The maximum current depends on the resistance of the tape and the acid and is of the order of 24 A in the existing set-up with the use of 100 μm thick, 1 cm wide Hastelloy tape. Currents of the order of 24 A are the upper limit due to resistive losses and resulting heating of the tape to temperatures in the range of 350 °C. In our new set-up with electrolytic contacts this limitation in the polishing current will be overcome.

With the present set-up the tape can be polished between 5 and 40 m h^{-1}. In our experiments the as-delivered tape[3] was spooled to reels and threaded into the EP apparatus. The acid temperature was set to 70 °C and the tape's speed was set to 15 m h^{-1}. The applied voltage was varied between 6 and 11 V, and the resulting current ranged between 10 and 22 A, respectively. The tape's surface area in the bath is 60 cm^2, which results in a mean surface current density in the range of 0.17 and 0.37 A cm^{-2}. Many EP experiments were conducted at different parameters with some 100 m of the same lot of Hastelloy tape. In this paper only the typical, reproducibly obtained results of two experiments at high and low polishing voltages/currents will be shown.

3. Polishing results and discussion

Figure 2(*a*) shows an optical micrograph of the unpolished, as-delivered tape, which was taken with differential interference contrast (DIC). Even if the starting material looks quite shiny to the eye, many grooves as a result of the rolling process and inclusions can be seen with the optical microscope. Atomic force microscope (AFM) measurements resulted in mean surface roughness values (R_a) of approximately 20 nm (averaged over 5 × 5 μm^2). For comparison figure 2(*b*) shows a DIC micrograph of the best mechanically polished tape obtained so far[4]. The R_a-value of this tape was measured to be 3.5 nm (averaged over 5 × 5 μm^2).

We performed a series of EP experiments with varying polishing currents/voltages at a bath temperature of 70 °C and a tape speed of 15 m h^{-1}. Figures 2(*c*) and (*d*) show the optical DIC micrographs of the tape surfaces from two different sets of EP experiments, which show typical results. The tape shown in figure 2(*c*) was polished at 6 V and 10 A (mean surface current density 0.17 A cm^{-2}). The rolling grooves have been smoothed, but are still apparent. Some grain boundaries become visible through the EP procedure. The R_a-value for this sample was measured by AFM to be 4 nm on a 5 × 5 μm^2 area. Even better results were obtained by using higher currents. Figure 2(*d*) shows the results with 11 V applied to the tape and 22 A polishing current (mean surface current density 0.37 A cm^{-2}). Almost no features besides some small hillocks can be seen on the surface. The grain boundaries are not visible in the micrograph shown as they are just below the resolution limit.

Figure 3 shows the results of AFM area scans on this tape. Grain boundaries are visible using this technique. The height differences of adjacent grains are of the order of 1 nm. The measured R_a-value is 0.5 nm on a 5 × 5 μm^2 area including the grain boundaries. The scanning of 5 × 5 μm^2 within larger grains avoiding grain boundaries results in a R_a-value of 0.3 nm. Figure 4 shows a comparison of AFM line scans on mechanically polished tape (figure 4(*a*)) and electropolished tape (11 V, 22 A) (figure 4(*b*)). On the mechanically polished tape, typical local slope angles are in the range of 5°. On

[1] Metfab Technologies Inc., Warwick, RI, USA.
[2] EPS 4000, Electro Polish Systems Inc., Brown Deer, WI, USA.
[3] Hamilton Precision Metals Inc., Lancaster, PA, USA.
[4] The mechanically polished tape was from a different lot than the unpolished and electropolished tapes.

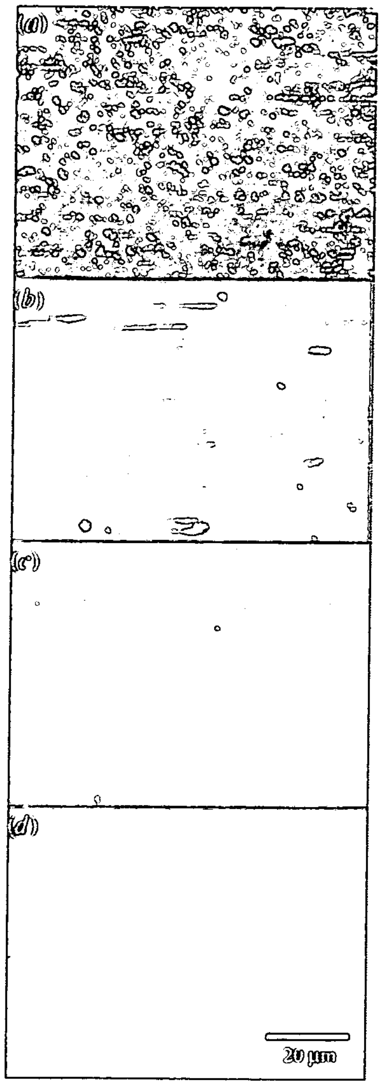

Figure 2. Optical micrographs of (a) the unpolished, (b) mechanically polished, (c) electropolished (6 V, 10 A) and (d) electropolished tapes (11 V, 22 A).

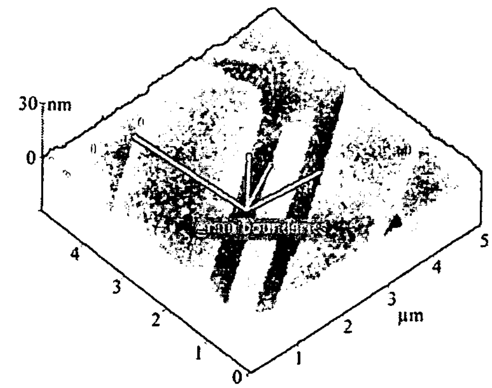

Figure 3. AFM scan of the surface of an electropolished tape. Polishing voltage 11 V, polishing current 22 A, tape speed 15 m h^{-1}.

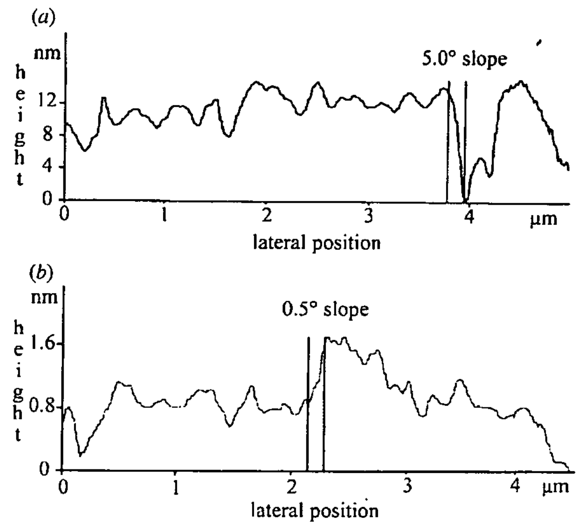

Figure 4. AFM line scans on mechanically polished tape (a) and electropolished tape (b) indicating typical slope angles.

Table 1. Typical R_a-values and local slope angle values of the Hastelloy tapes.

Preparation	R_a-value (nm)	Typical slope
Unpolished	20	5°
Mechanically polished	3.5	5°
Electropolished (6 V, 10 A)	4	1.5°
Electropolished (11 V, 22 A)	0.5	0.5°

the electropolished tape, the typical slope angles are 0.5° and therefore smaller by one order of magnitude. Occasionally, grain boundaries have slopes exceeding 0.5°.

The two electropolished tapes (figures 2(c) and (d)) show evidence for a strong dependence of the polishing result on the applied voltage, polishing current and the tape speed as could be verified in further experiments. Obviously, the higher currents are needed to obtain a smooth surface finish. Very low polishing currents resulted in a strong etching of the grain boundaries with high local slope angles and big differences in the height of the grain surfaces in the range of several nanometres between adjacent grains. Slow speeds, and therefore long polishing times, at higher polishing currents had a similar effect of making the grain boundaries more pronounced. However, the differences in heights of the adjacent grains are less. A parameter window for obtaining smooth surfaces without enhancing the grain boundaries too much seems to exist. More detailed examinations on the EP process and the influence of polishing current and tape's speed will be presented in the future.

For comparison, typical results obtained are shown in table 1. Both mechanically polished and unpolished Hastelloy tapes show local slope angles in the range of 5°, but the mechanically polished tape is significantly smoother. The electropolished tape with low polishing current has a surface roughness comparable to the mechanically polished tapes, but the mean local slopes are less steep. The best results were

obtained for the density electropolished at high current tape. A R_a-value of 0.5 nm and a mean local slope angle of 0.5° are evidence of very smooth surfaces on a nm-scale.

4. Deposition experiments on electropolished substrates

IBAD-MgO layers were produced on a set of electropolished tapes by a continuous deposition process. However, the results are still at a preliminary stage. On several metres of EP tape (polished at 6 V, 10 A) continuous IBAD-MgO layers show FWHM (full width at half maximum) values for the in-plane orientation between 5.5° and 7°. The best results on mechanically polished tapes thus far had been 7.1° to 9.5° in-plane FWHM [8]. Therefore a significant improvement could be obtained by depositing on surfaces with smaller slope angles. Experiments on even smoother tapes are still underway. The out-of-plane orientation was measured to be 2.8° FWHM, which compares to the best values obtained on mechanically polished tapes. A YBCO coating on an electropolished tape/IBAD-MgO sample resulted in a critical current density of 1.5 MA cm^{-2} (75 K, 0 T) at a film thickness of 1.65 μm. This first result is already in the range of the best results obtained on IBAD-MgO so far [9]. Therefore further improvement is expected in the future.

5. Conclusions

Optimized electropolishing of Hastelloy substrate tapes has proved to result in smooth surfaces with very shallow slope angles. Mean surface roughness values R_a of 0.5 nm on 5 × 5 μm^2 areas were obtained and the local slope angles were decreased to 0.5°. IBAD-MgO coating experiments resulted in an improved in-plane alignment of the MgO layer and subsequent YBCO depositions yielded high critical current densities of the YBCO layer. Therefore, electropolishing is an attractive alternative to the process of mechanical polishing and seems to be a viable route for the industrial scale-up of coated conductor fabrication.

Acknowledgments

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